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Photoreactivity of Selected Aromatic Hydrocarbons in Water

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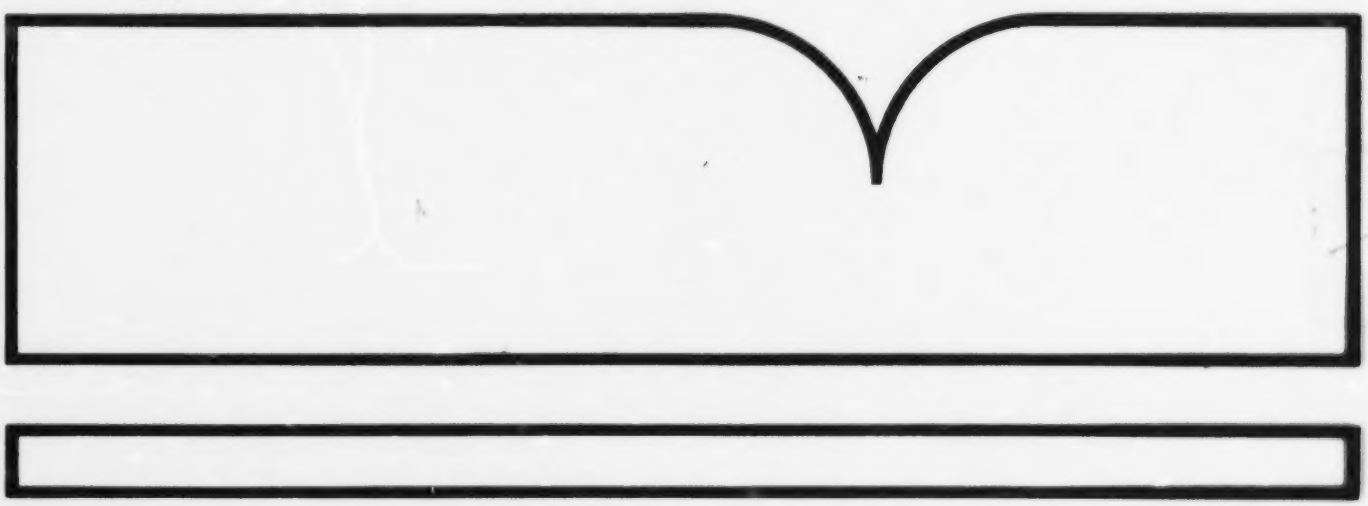

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POLYNUCLEAR AROMATIC HYDROCARBONS

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16. ABSTRACT

Quantitative data concerning photoreactions of aromatic hydrocarbons were obtained in distilled water and several natural water samples. The reactions were studied at concentrations lower than the solubility limits of the aromatics, which in some cases were less than 1 microgram per liter. At these low concentrations, the photolyses were described by first-order rate equations, i.e., half-lives,were concentration-independent. Quantum yields and electronic absorption spectra were obtained for a series of naphthalenes, anthracenes, and polycyclic aromatics. These data were used in conjunction with simulated solar spectral irradiance and attenuation coefficients of water bodies to compute photolysis half-lives for the aromatic hydrocarbons in aquatic environments having varying depths and turbidities.

17. KEY WORDS AND DOCUMENT ANALYSIS

DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Quantum efficiencies		06F
Photolysis		07E
Contaminants		07D
Water		13B
Half-life		18B
Aromatic polycyclic hydrocarbons		68D

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PHOTOREACTIVITY OF SELECTED AROMATIC HYDROCARBONS IN WATER

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INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH) are known to be widespread contaminants of natural water bodies (1). Several hydrophobic PAH such as benzo[a]pyrene (B[a]P) are known carcinogens that have been shown to bioaccumulate in aquatic organisms (23). The more water-soluble bicyclic and tricyclic PAH are not carcinogenic, but recent studies indicate that ultraviolet radiation transforms some of these chemicals into products that are acutely toxic to a variety of aquatic organisms (15).

Concern over the environmental safety and persistence of PAH has prompted studies of processes that transport and transform these chemicals in natural waters. Microbial oxidation is most rapid with benzene and naphthalene and with their alkylated derivatives (7). Tricyclic and especially higher molecular-weight polycyclic aromatics such as B[a]P are considerably more resistant to degradation by microorganisms. Recent studies in an outdoor model ecosystem indicated to Lee and co-workers that photochemical transformation is an important process for several PAH including B[a]P (16).

Although a great deal is known about the photochemistry of aromatic compounds in solution, most past studies have been carried out in organic solvents at high concentrations with oxygen present (9). Under these reaction conditions, direct and indirect (photosensitized) oxygenation are important. Direct photooxygenation is initiated through light absorption by the aromatic compound. Indirect photooxygenation occurs via light absorption by another chemical, called a photosensitizer, that has been added to the system in addition to the aromatic compound. Although a variety of mechanisms have been proposed since these studies began some 50 years ago, it is now generally

accepted that singlet oxygen, an excited form of molecular oxygen, is the key intermediate in photooxygenations.

Analytical difficulties associated with the low solubilities of PAH have limited study of their photochemistry in water. Indeed, comprehensive data concerning the aqueous solubilities of the higher-molecular weight PAH have not become available until very recently (17). It has been suggested that the PAH in aquatic environments are completely sorbed to particulate matter (23). Recent studies by Wolfe *et al.* (31), Smith *et al.* (25) and Karickhoff and co-workers (12), however, have demonstrated that sorption of PAH and other chemicals to natural sediments and biogenous material is a reversible equilibrium process and that it is likely that the PAH in the water columns of many inland water bodies and in the ocean exist mainly in the dissolved state. Andelman and Suess (2) and McGinnes (18) established that the PAH, B[a]P and benz[a]anthracene are photoreactive in aqueous media, although interpretation of their results was clouded by the presence of acetone, a known photosensitizer, in their reaction media. More recently, Smith and co-workers (25) have reported kinetic data concerning direct photolysis in water of several aromatic compounds that are found in effluents of fossil-fuel processing plants. In this paper, we present detailed studies concerning the photoreactivity in water of several PAH that are commonly found in environmental samples (8). The effects of light attenuation and sediment-water partitioning on the photolysis of PAH in the aquatic environment are also discussed.

EXPERIMENTAL

Materials

1-Methyl and 2-methylnaphthalenes of greater than 99% purity were obtained from Chemical Samples Co. 9-Methylanthracene, 9,10-dimethylanthracene and chrysene were analytical grade (> 99% pure) obtained from K&K Laboratories. Fluoranthene and naphthacene (> 99%) were obtained from Analabs. Reagent-grade pyrene and phenanthrene were purified by elution chromatography on neutral alumina with subsequent recrystallization from 95% aqueous ethanol. Anthracene and naphthalene (reagent) were each recrystallized from 95% aqueous ethanol prior to use. Laboratory distilled water was redistilled from permanganate and a middle cut was retained for these studies. Spectro-grade isooctane from Burdick and Jackson Co. was used as received. Natural water samples were obtained from the top meter of the water column and stored at 5°C prior to use.

Procedures

Reaction mixtures were analyzed using a Micromeritics Liquid Chromatograph with variable-scan UV-detection or a Farrand MK-1 Spectrofluorometer as detector. An ODS-1 column with methanol-water as the mobile phase was used.

A "merry-go-round" photochemical apparatus that is described by Moses *et al.* (21) was employed for the kinetic studies. Quantum yields for reaction were computed from the slopes of plots of natural log concentration versus time as previously described (32). Light from a 450-W medium-pressure mercury lamp was filtered as follows: 313 nm, a solution of 0.001 *M* potassium chromate and 3% potassium carbonate in conjunction with 4 mm thick pyrex glass; 366 nm, Corning 7-54 and 0-51 filter combination; 436 nm, Corning 3-73 and 5-58 glass filter combination. The light intensity was monitored by the potassium ferrioxalate actinometer (0.15 *M*) at 366 nm and 436 nm (10). The benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene was employed as an actinometer for 313-nm light (13). All studies were conducted at concentrations lower than the solubility limits (17). The reaction cells were cleaned by aqua regia and rinsed with dilute ammonium hydroxide, then distilled water prior to use; this procedure minimized problems with adsorption of the PAH to the cell walls. Degassing was accomplished by three freeze-pump-thaw cycles with the reaction cells attached to a vacuum rack. The cells were sealed under a vacuum of 10^{-3} mm Hg.

Electronic absorption spectra were obtained using a Perkin-Elmer Model 356 Spectrophotometer employing cells with a calibrated pathlength. Spectra of naphthacene, chrysene and phenanthrene were obtained in water-methanol mixtures.

Rate constants for direct photolysis in the aquatic environment were calculated using a computer program that was previously described (33). The program was modified to permit computation of rate constants at points of various depths in a water body with specified diffuse attenuation coefficients.

RESULTS AND DISCUSSION

Direct Photolysis of PAH

Kinetic data for the direct photochemical reactions in water of all the aromatics studied could be described by a first-order rate equation. Disappearance quantum yields, ϕ_r, were computed from the slopes of the first-order plots (Table I) (32). In general, quantum efficiencies were determined at a wavelength that closely corresponded to that of maximum sunlight absorption by the PAH (*vide infra*). Most of the quantum yields were in the

TABLE I. Kinetic Data for Direct Photochemical Reactions of Polycyclic Aromatic Hydrocarbons in Air-Saturated Water at 25°C

Aromatic Compound	Wavelength (nm)	$10^7 \times [A]$ [a] (M)	$10^3 \times \epsilon$ [b] (1/gmole cm)	$10^3 \times \phi_r$ [d]
Naphthalene	313	1.2×10^3	0.11 ± 0.005	15 ± 1
1-Methylnaphthalene	313	1.2×10^3	0.28 ± 0.01	18 ± 1
2-Methylnaphthalene	313	8.8×10^2	0.26 ± 0.01	5.3 ± 0.2
Phenanthrene	313	8.4	0.20 ± 0.01[c]	10 ± 1.6
Anthracene	366	2.3	2.1 ± 0.1	3.0 ± 0.2
9-Methylanthracene	366	3.1	9.9 ± 0.2	7.5 ± 0.5
9,10-Dimethylanthracene	366	1.3	4.0 ± 0.3	4.0 ± 0.4
Pyrene	313	3.9	8.8 ± 0.4	2.0 ± 0.3
Pyrene	366	3.9	0.19 ± 0.01	2.2 ± 0.3
Fluoranthene	313	6.6	3.8 ± 0.2	0.12 ± 0.01
Fluoranthene	366	6.6	3.5 ± 0.2	0.002 ± .0002
Chrysene	313	8.2×10^{-2}	7.4 ± 0.2[c]	2.8 ± 0.7
Naphthacene	436	2.2×10^{-2}	6.1 ± 0.2[c]	13 ± 5

[a] PAH concentration
[b] Molar absorptivity in water.
[c] Obtained in 50% water-methanol.
[d] Disappearance quantum yield; mean of triplicate determination ± standard deviation.

0.001 to 0.01 range. More detailed wavelength studies were conducted with pyrene and fluoranthene because they are both abundant PAH in environmental samples (8). The disappearance quantum efficiency of pyrene exhibited the usual wavelength independence. However, ϕ_r for fluoranthene dropped sharply in going from 313 to 366 nm. Even at 313 nm, fluoranthene photoreacted considerably less efficiently than the other PAH included in this study. Peculiar excited-state behavior has also been observed of fluoranthene in spectroscopic studies (3). The anomolous photochemical behavior is probably related to the fact that fluoranthene, unlike the other PAH studied, is a nonalternant aromatic hydrocarbon (3).

Prior studies (2,9,25,29) suggested that the direct photolysis of PAH in water would involve photooxygenation mediated by singlet oxygen formed by energy transfer from the electronically excited aromatic molecule in its triplet state. Stevens and co-workers (28-30) derived the following equation (Equation 1) for quantum yields of direct photooxygenation, ϕ_{AO_2}.

$$\phi_{AO_2} = \phi_T \{([A] + p\beta)/([A] + \beta\} \quad (1)$$

The term ϕ_T is the intersystem crossing efficiency (4,24), β is a reactivity index that is inversely proportional to the rate constant for reaction of singlet oxygen with the aromatic compound (6,19), and $p\beta$ is a solvent-dependent constant that approximately equals 8×10^{-5} mole/l in water (29). At the low PAH concentrations that were employed in this study, ϕ_{AO_2} is concentration-independent. Values of ϕ_{AO_2} were computed for several PAH and are compared to ϕ_r for the compounds in Table II. The comparison indicates that photooxygenation involving singlet oxygen typically accounts for a negligible fraction of the observed photoreactions, even for PAH, naphthacene and 9,10-dimethylanthracene, compounds that have the largest ϕ_{AO_2} values.

Quantum efficiencies for reaction of naphthalene, anthracene, pyrene and naphthacene were observed to be 10 to more than 100 times smaller in air-saturated isooctane than in water, indicating that the observed reaction is strongly dependent on solvent polarity. This solvent effect suggested that the reactions in water may be initiated by electron transfer to oxygen, a "Type I" photooxidation (6) that certainly would be enhanced in polar solvents. However, careful removal of dissolved oxygen by degassing (oxygen concentration less than 10^{-9} *M*) had no effect upon the photolysis rate of 9-methylanthracene (Figure 1). Andelman and Suess (2) and Smith *et al.* (25) have likewise found that photochemical transformations of benzo[a]pyrene, benz[a]anthracene and some heterocyclic aromatics occur in water in the absence of molecular oxygen. We also found that the 9-methylanthracene reaction was unaffected by the presence of 1.2×10^{-3} *M* mercuric chloride,

TABLE II. Comparison of Observed Quantum Yields for Reaction of PAH in Air-Saturated Water (ϕ_r) with Computed Quantum Efficiencies for Photooxygenation (ϕ_{AO_2})

Aromatic Compound	ϕ_r	Assumed[b] ϕ_T	$\beta_{H_2O}\,M$[e]	ϕ_{AO_2}	$\frac{\phi_{AO_2}}{\phi_r}$
Naphthalene	1.5×10^{-2}	0.86[c]	10^8	7×10^{-13}	5×10^{-11}
Phenanthrene	1.0×10^{-2}	0.87[d]	10^8	7×10^{-13}	7×10^{-11}
Anthracene	3.0×10^{-3}	0.70[c]	3.2	1.8×10^{-5}	6×10^{-3}
9-Methylanthracene	7.5×10^{-3}	0.67[d]	1.6×10^{-1}	3.3×10^{-4}	4×10^{-2}
9,10-Dimethylanthracene	4.0×10^{-3}	0.11[d]	2.4×10^{-2}	3.6×10^{-4}	9×10^{-2}
Chrysene	2.8×10^{-3}	0.83[d]	10^8	7×10^{-13}	2×10^{-10}
Naphthacene	1.3×10^{-2}	0.84[d]	4.1×10^{-2}	1.6×10^{-3}	1×10^{-1}
Benz[a]anthracene	3.3×10^{-3}[a]	0.80[d]	1.0×10	6.4×10^{-6}	2×10^{-3}
Benz[a]pyrene	8.9×10^{-4}[a]	0.7[c]	2.4×10^{a}	2.3×10^{-6}	3×10^{-3}

[a] Smith and co-workers (25).
[b] Assumed to equal one minus fluorescence quantum efficiency.
[c] Schwarz and Wasik (24).
[d] Birks (4).
[e] Stevens *et al.* (30) except where noted; corrected for differences in lifetime of singlet oxygen in benzene and water (19).

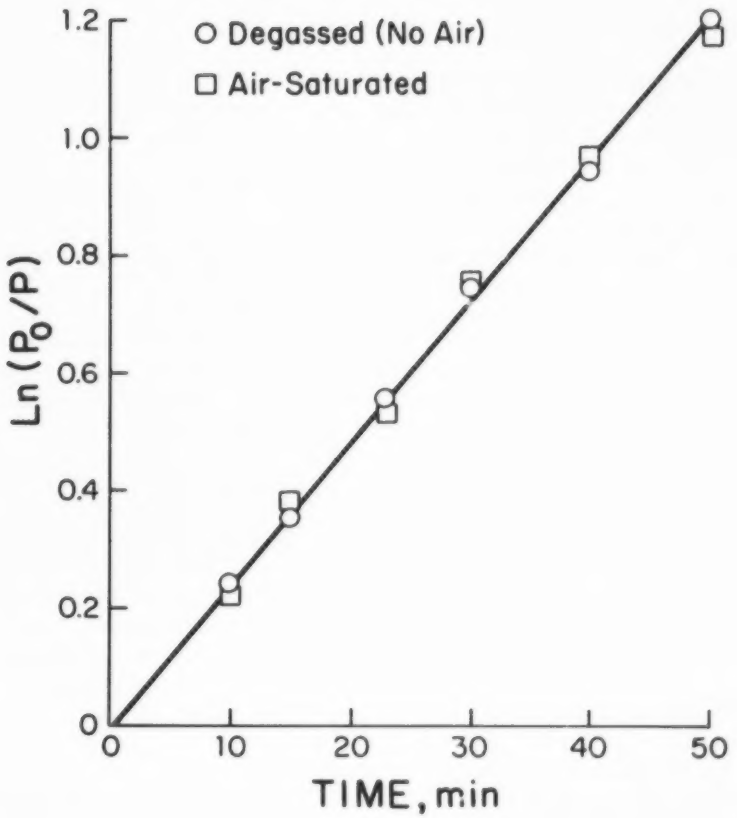


FIGURE 1. Effect of oxygen removal upon direct photolysis (313 nm) of 9-methylanthracene in water.

a known triplet-state quencher (22). Thus, the reactive species is either the excited singlet state or, perhaps, a short-lived upper-triplet state.

Taken together, these kinetic studies suggest that the predominant primary photochemical processes of PAH in water may not involve molecular oxygen. Product studies are being conducted to elucidate the mechanism of these photoreactions. Other studies have demonstrated that aromatic compounds, such as benzene (11), undergo photohydrolysis in water (5). The large change in reaction quantum efficiency in going from nonpolar organic solvents to water suggests that the reactions may involve photoionization to form radical cation intermediates.

Predicted Photolysis Rates of PAH in Natural Water Bodies

The photolysis rate, *i.e.*, conversion per unit time ($-d[A]/dt$) of an aromatic hydrocarbon in a water body at depth z, can be described by Equation 2:

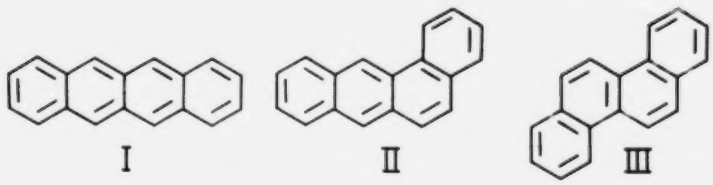
$$\left(\frac{d[A]}{dt}\right)_{z,\lambda} = \Sigma \phi_{r,\lambda}\, k_{z,\lambda}\, [A] = k_{p,z}[A] \qquad (2)$$

where $\phi_{r,\lambda}$ is the quantum yield at wavelength λ and $k_{z,\lambda}$ is the specific sunlight absorption rate of the aromatic at wavelength λ and depth z (20). The total rate is obtained by integrating over the effective range of wavelengths (32). The $k_{z,\lambda}$ value is essentially a measure of the spectral overlap between the electronic absorption spectrum of the aromatic compounds and the solar irradiance reaching depth z. We have also found it convenient to define a related term, k_a, that is the *average* specific sunlight absorption rate of a pollutant in a water column of depth z (33). A computer program has been developed that can be used to approximately calculate solar spectral irradiance as a function of time, location and depth in a water body (33). The program uses the simulated irradiance values, quantum yields and the molar absorptivities of chemicals to compute their photolysis rates in natural water bodies. The computed photolysis rate constants, k_p, have been shown to be in close agreement with k_p values obtained from experiments under sunlight (25,33). Some representative half-lives, $0.693/k_p$, for direct photolysis of PAH in water are shown in Table III. The half-lives were computed for a clear day near the surface of a water body where the chemical is fully exposed to sunlight. Effects of light attenuation will be discussed later. Although the photoreactions are very inefficient, with typically less than 1% of the energy absorbed resulting in photoreaction, conversion under sunlight for most of the PAH studied is rapid because sunlight absorption rates are generally very large. Interestingly, the naphthalenes have among the highest disappearance quantum efficiencies but about the lowest photolysis rates. This seeming anomaly is attributable to the much lower sunlight absorption rates of the naphthalenes, which weakly absorb only the less-intense UV-B (280-320 nm) part of solar radiation. Note that there is a ragged trend of increasing photoreactivity with increasing molecular weight; the opposite is the case with microbial oxidation (7,16). This trend is mainly caused by the enhanced spectral overlap of the absorption spectra of the high-weight aromatics with solar radiation. The "bent" PAH, *e.g.*, phenanthrene and chrysene, are less photoreactive than their linear isomers. This effect is best illustrated by comparing half-lives of the isomers, naphthacene (I), benz[a]anthracene (II) and chrysene (III); each "bend" increases the half-life by about an order of magnitude (Table III).

TABLE III. Computed Near-Surface Half-Lives for Direct Photochemical Transformation and Photosensitized Oxygenation of Several Aromatic Hydrocarbons (latitude 40°N, midday, midsummer)

Compound	$10 \times k_a$ (sec^{-1})[a]	λ (nm)[b]	Half-Life (hr)[c]	
			Direct	Photosensitized[d]
Naphthalene	0.0018	310	71	10^9
1-Methylnaphthalene	0.0048	312	22	
2-Methylnaphthalene	0.0069	320	54	
Phenanthrene	0.023	323	8.4	10^9
Anthracene	0.83	360	0.75	2.0×10^2
9-Methylanthracene	2.0	380	0.13	1.0×10
9,10-Dimethylanthracene	1.4	400	0.35	1.5
Pyrene	1.4	330	0.68	
Fluoranthene			21[f]	
Chrysene	0.22	320	4.4	10^9
Naphthacene	4.3	440	0.034	2.6
Benzo[a]pyrene[e]	4.0	380	0.54	1.5×10^3
Benz[a]anthracene[e]	0.99	340	0.59	6.4×10^2

[a] Specific sunlight absorption rate (33).
[b] Approximate wavelength of maximum sunlight absorption.
[c] Period of exposure required for 50% conversion.
[d] Computed by Equation 3 assuming $[O_2^*]$ is 6×10^{-12} mole/l.
[e] Reference 25.
[f] Based on photolysis under sunlight.



Although the data in Table II indicated that direct photooxygenation of the PAH is insignificant, the possibility still existed that photosensitized oxygenation involving singlet oxygen might be important in natural water. Recent studies have indicated that the photosensitized generation of singlet oxygen is a general phenomenon in the aquatic environment (34). To evaluate the potential importance of photosensitized oxygenation of PAH dissolved in natural waters, rate constants and half-lives for the reactions were computed by Equation 3 (34) where the values of k_A, the rate constants

$$t_{1/2} = \frac{0.693}{k_A\ [^1O_2{}^*]} \tag{3}$$

for reaction of singlet oxygen with the aromatic hydrocarbons, were obtained from studies of Stevens *et al.* (30) and Smith and co-workers (25), and the near-surface steady-state concentration of singlet oxygen $[^1O_2{}^*]$ was assumed to equal 6×10^{-12} *M* in summer (34). Comparisons of half-lives for direct photolysis and photosensitized oxygenation of the PAH that were studied (Table III) indicate that the former process is considerably more rapid. Thus, photosensitized oxygenation of these PAH is essentially negligible. It should be pointed out that these considerations apply only to PAH dissolved in the water. Larson and Hunt (14) have shown that singlet oxygen is involved in the photooxidation of aromatics dissolved in petroleum films.

To further evaluate the potential importance of photosensitized reactions in natural water, the photolysis of pyrene was studied in water samples obtained from the Gulf of Mexico at Shell Point, Florida, and the Aucilla River at Lamont, Florida. The Aucilla River is a "black water" system that strongly absorbs ultraviolet and visible light; concentrations of singlet oxygen that form when it is exposed to sunlight are among the highest that have been observed in natural waters (34). The observed photolysis rate constant of pyrene was the same at 313 nm in the Gulf of Mexico water as in distilled water (Figure 2) and nearly the same in the Aucilla River water. Similar results were obtained when the solutions were exposed to sunlight. The Aucilla River data, when corrected for the expected retardation caused by light screening by the UV-absorbing substances in the water, indicated that some acceleration,

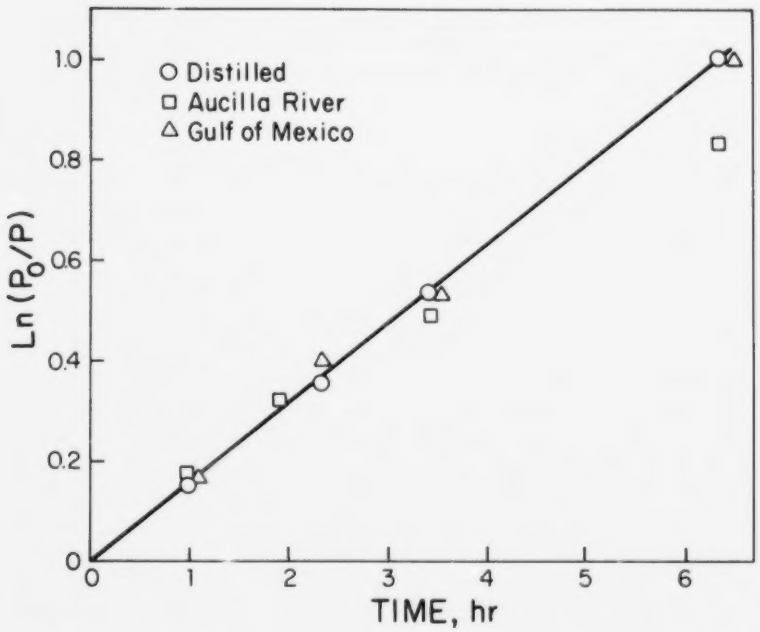


FIGURE 2. Kinetic data for photoreaction (313 nm) of pyrene in distilled water and in two natural water samples.

perhaps photosensitization, was occurring. This effect, however, could also have been caused by a twofold enhancement of the quantum efficiency for direct photolysis. Most significant was the fact that the photolysis rates were nearly the same in both natural and distilled water. Similar observations have been reported for other PAH by Smith and co-workers (25). Dark controls of pyrene in the natural water indicated no microbial degradation over a 10-day period.

Effects of Light Attenuation and Partitioning

Thus far, only factors that determine the photoreactivity of PAH have been discussed. Any assessment of the role of photolysis in a natural water body must also take into account the dose of light that the polycyclic aromatic is likely to receive. Factors influencing the amount of sunlight reaching the earth's surface are discussed in many places (see Reference 33 for lead

references). In this section, typical effects of light attenuation and partitioning to biota or sediments are discussed. The procedures used below in making these assessments are discussed more thoroughly elsewhere (20,32,33).

The Sea

The attenuation of solar radiation in a water body is best described in terms of diffuse attenuation coefficients, K_λ, where K_λ is the slope of a logarithmic (Napierian) plot of solar irradiance at wavelength λ versus depth (27). Solar irradiance $I_{z,\lambda}$ at depth z approximately equals $W_\lambda e^{-K_\lambda z}$ where W_λ is the surface irradiance. Diffuse attenuation coefficients for the sea increase with decreasing wavelength in the blue and ultraviolet spectral region where most PAH absorb light. Thus, the decrease in direct photolysis rates of polycyclic aromatics with increasing depth is more pronounced for those PAH that absorb shorter wavelengths of light. This effect is illustrated in Figure 3 for naphthalene, anthracene and naphthacene–PAH that absorb in the UV-B, near-UV, and visible region, respectively (Table III). The depth profiles of Figure 3A were computed for clear ocean water of low productivity in the middle of the Gulf of Mexico employing simulated solar spectral irradiance for cloudless days at the water surface (33) and diffuse attenuation coefficients recently reported by Smith and Baker (26). The profiles computed for the same PAH in moderately productive coastal waters near Tampa,

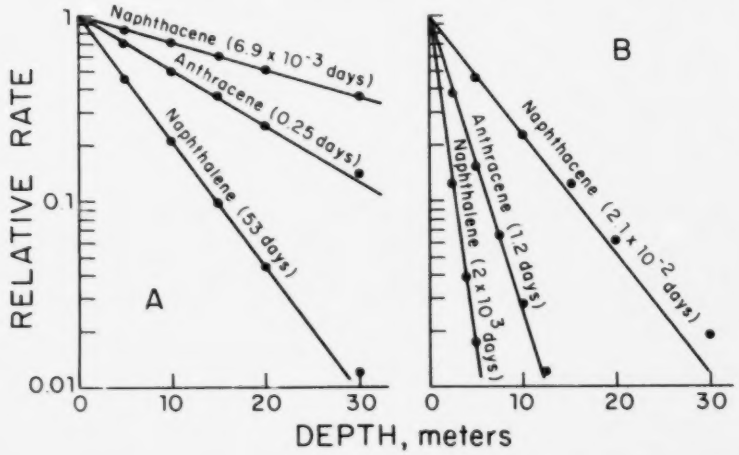


FIGURE 3. Computed depth dependence for direct photolysis of several PAH during summer in the Gulf of Mexico: (A) Mid-Gulf; (B) coastal water near Tampa, FL. Average half-lives in top 35 m are in parentheses.

Florida (26), during October 1977 are illustrated in part B of Figure 3; it was assumed that the algae were uniformly distributed in the water column. Average half-lives inherent to direct photolysis were computed for the PAH in the top 35 meters (Figure 3). The rate constants employed in the half-life calculations were integrated over the full day so that photolysis could be compared to other processes that are not light-dependent. Examination of the data in the figure indicates that direct photolysis of many of the PAH examined in this study is rapid throughout the mixed layer of the ocean. Direct photolysis is generally slower in coastal than in mid-Gulf water, particularly for naphthalene, a UV-B absorbing compound. Smith and Baker (26) attribute the strong light attenuation in the UV-B region mainly to unusually high concentrations of dissolved organics in the coastal water. Several "black water" rivers, *e.g.*, the Suwannee River, drain into the Gulf of Mexico near Tampa. Ultraviolet radiation is not attenuated as strongly in California coastal waters (26).

The above considerations pertain to PAH that are completely dissolved in the sea. Available evidence, discussed in the introduction of the paper, indicates that a large fraction of the PAH that enter the ocean from the atmosphere or a small oil spill become dissolved in the ocean water. A small fraction bioaccumulates in the algae or other biogenous material. With a major oil spill it is likely that the oil-to-water ratio in the mixed layer of the ocean would initially be so high that most of the high-weight PAH would remain in the oil phase. Because sorption to oil is almost certainly a rapidly reversible equilibrium process, however, the PAH would progressively move into the seawater from the oil phase as the oil becomes diluted.

Inland Waters

Light attenuation is much more pronounced in inland water bodies than in the ocean (20,33). Moreover, a portion of the PAH in rivers and lakes partitions into the bottom sediment where no light is present (8).

To approximately assess the effects of this partitioning on the overall rate of loss by photochemical transformation in a river, the following assumptions are made. First, it is assumed that the water body is well mixed and that the PAH dissolved in the water column are equilibrated with the PAH sorbed to suspended sediments and the top layer of bottom sediments. Thus, as the PAH in the water column photodegrade, more PAH are rapidly released to maintain equilibrium. Second, it is assumed that the partitioning can be quantitatively described in terms of a partition coefficient K_p. This coefficient equals $P_s(P_w\rho)^{-1}$ where P_s and P_w are the amounts of dissolved and sorbed PAH per unit volume in the system and ρ is the weight ratio of dry sediment to water. Karickhoff *et al.* (12) have shown that the K_p values for several PAH can be approximately computed using Equation 4.

$$K_p = 0.63\, F_f\, F_{oc} P \qquad (4)$$

where F_f = the dry weight fraction of clay and silt-sized particles in the sediment
F_{oc} = the fractional mass of organic carbon in the sediment
P = the octanol-water partition coefficient of the aromatic compound.

It can be shown that partitioning to the bottom sediment slows photolysis (31) by a factor of $(1 + K_p\rho)$ if degradation of the PAH in the sediment is very slow, an assumption that is certainly valid for the higher-molecular weight PAH (7,16,25).

For illustrative purposes, average photolysis rate constants were computed for several PAH in a 5-m-deep well-mixed water body that contained a mean sediment concentration of 20 mg/l (Table IV). This sediment concentration is the average observed in the Ohio River at Cincinnati during the summer (20). The diffuse attenuation coefficient that correspond to the assumed sediment concentration is estimated to be about 11 m^{-1} at 330 nm (20). In computing the rate constants in the table, this attenuation coefficient was assumed for all the PAH, an assumption that probably overestimates light attenuation for most PAH. To permit the rate constants to be better visualized, they have been transformed into half-lives. It is stressed that the term half-life has no meaning in a flowing system with continual inputs as is usually the case with rivers polluted by PAH. To demonstrate the potential "buffering" effect of sediment-water exchange, two sets of rate constants were computed. The first set was computed assuming that the PAH are completely in the water column and the photolysis rates are affected only by light attenuation. It can be readily shown using the K_p values in Table IV, that the PAH in the water column are almost completely dissolved, not sorbed to the suspended sediments; ρ for the suspended sediment is only 2×10^{-5}. The second set of half-lives were computed for photochemical loss of PAH in the same system, but with rapid exchange between the top centimeter of the bottom sediment and the water column. This exchange could involve continual sedimentation and resuspension of the top layer of the bottom sediment. The K_p values for the sediment were computed from octanol-water partition coefficients (Equation 4 assuming that $F_{oc} = 0.015$ and $F_f = 0.5$). The bottom sediments are usually about half water so ρ is assumed to be 0.001.

Results in the table indicate that partitioning to the bottom sediment has the most pronounced effect on photolysis of the higher molecular weight PAH, which have the greatest tendency to sorb. The calculations further suggest that, of the PAH studied, anthracene and naphthacene should be the most susceptible to photochemical transformation in a deep inland water body. Obviously, the above assumptions concerning partitioning are greatly oversimplified. At present, there is little information available on rates of bottom sediment-water column exchange for organic pollutants.

TABLE IV. Illustrative Effects of Light Attenuation and Sediment-Water Partitioning on Direct Photolysis of Several PAH in a 5-m-deep Inland Water Body[a]

Compound	$P \times 10^{-3}$ [b]	K_p [d]	$(1 + K_p \rho)^{-1}$ [e]	Half-Life (days)[f]	
				No Partitioning	With Partitioning
Naphthalene	2.3	4.7	0.99	550	550
1-Methylnaphthalene	13	61	0.94	180	190
2-Methylnaphthalene	13	61	0.94	410	440
Phenanthrene	37	180	0.85	59	69
Anthracene	35	160	0.86	4.5	5.2
9-Methylanthracene	117	550	0.64	0.79	1.2
Fluoranthene	60[c]	280	0.78	160	200
Pyrene	84	400	0.71	4.2	5.9
Benz[a]anthracene	310[c]	1,500	0.40	3.7	9.2
Chrysene	880[c]	4,200	0.19	13	68
Naphthacene	800	3,800	0.21	0.20	0.95
Benzo[a]pyrene	650[c]	3,100	0.24	3.2	13

[a] Assumptions: Suspended sediment concentration, 20 mg/l; diffuse attenuation coefficient, 11 m^{-1}
[b] From Karickhoff *et al.* (12) except where noted.
[c] Computed from water solubility (12).
[d] Computed using Equation 13.
[e] Fraction dissolved in water column including partitioning to top cm of bottom sediment.
[f] Integrated over full summer day, latitude 40° N.

SUMMARY

These studies indicate that many of the higher molecular weight polycyclic aromatics are rapidly transformed in water by the action of sunlight. The naphthalenes, fluoranthene and phenanthrene photolyze slowly. Surprisingly, with at least some of the PAH, the disappearance quantum efficiencies are unaffected by molecular oxygen. The photoreactions are considerably more efficient in water than in hydrocarbon solvents. Photosensitized oxygenation of PAH dissolved in natural waters appears to be too slow to compete with direct photolysis. Thus, excluding photoreactions in petroleum slicks, it does not appear that singlet oxygen plays a significant role in the photochemical transformation of PAH in the aquatic environment.

Computations indicate that photoreactions of many PAH are rapid throughout the upper, mixed layer of the ocean (top 35 meters). In turbid rivers, however, photolysis is greatly slowed via light attenuation and partitioning of the PAH to bottom sediments where no light is present. Higher molecular weight PAH are most susceptible to the latter effect.

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DISCLAIMER

Mention of trade names or commercial products does not necessarily constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

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